

**CHIRAL DIPHOSPHORUS COMPOUNDS AND THEIR
TRANSITION METAL COMPLEXES**

BACKGROUND OF THE INVENTION

5 Field of the Invention: The present invention relates to chiral diphosphorus compounds and their transition metal complexes, to a process for preparing chiral diphosphorus compounds and their transition metal complexes and also to their use in asymmetric syntheses.

10 Brief Description of the Prior Art: Enantiomerically enriched chiral compounds are valuable starting substances for preparing agrochemicals and pharmaceuticals. Asymmetric catalysis for the synthesis of such enantiomerically enriched chiral compounds has gained great industrial significance.

15 The multitude of publications in the field of asymmetric synthesis shows clearly that transition metal complexes of diphosphorus compounds are particularly suitable as catalysts in asymmetric reactions. In particular, transition metal complexes of diphosphorus compounds have found use in
20 industrial processes as catalysts in asymmetric hydrogenations of C=O, C=N and C=C bonds, hydrocyanations and hydroformylations.

For instance, US Patent 5,175,335; Rajan Babu, J. Am. Chem. Soc., 1996, 118, 6325-6326 and Rajan Babu, J. Org. Chem., 1997, 62, 6012-
25 6028 disclose the use of enantiomerically enriched 1,6-substituted 3,4-(bisphosphinito)tetrahydrofurans and their transition metal complexes for asymmetric hydrocyanations and hydrogenations.

The use of the enantiomerically enriched 3,4-(bisphosphino)
30 tetrahydrofurans and their transition metal complexes in asymmetric hydrogenations is also disclosed by EP-A 885 897 and A. Terfort,

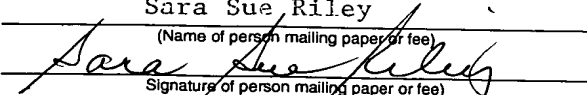
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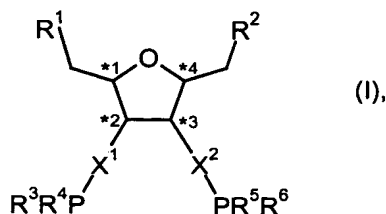
Synthesis, 1992, 10, 951-953. Enantiomerically enriched 3,4-(bisphosphito)tetrahydrofurans are described, for example, in W. R. Jackson, Aust. J. Chem., 1982, 35, 2069-2075 and, 3,4-(phosphinophosphito)tetrahydrofurans in A. Kless, Tetrahedron: Asymmetry, 1996, 7, 33-36.

The disadvantage of all of the enantiomerically enriched 3,4-(diphosphorus)-tetrahydrofurans mentioned is that steric and electronic variation of the central tetrahydrofuran framework, which is necessary for precise optimization and adaptation of the ligand and therefore of the catalyst for a given substrate, is only possible to a very limited extent and by numerous, complex synthetic steps. These disadvantages make industrial utilisation of such ligands and the catalysts preparable therefrom uneconomic.

There is therefore a need to develop a ligand system whose steric and electronic properties can be easily varied, and whose transition metal complexes as catalysts in asymmetric synthesis, in particular asymmetric hydrogenations, enable not only high enantioselectivity but also high conversion rates.

SUMMARY OF THE INVENTION

Diphosphorus compounds of the formula (I) have now been found



where

*1, *2, *3 and *4 are each independently a stereogenic carbon atom which is in the R- or S- configuration,

X¹ and X² are each independently absent or are oxygen and

R¹ and R² may each independently be: hydrogen, C₁-C₂₀-alkyl, C₁-C₂₀-fluoroalkyl, C₂-C₂₀-alkenyl, C₄-C₂₄-aryl, C₅-C₂₅-arylalkyl, C₆-C₂₆-arylalkenyl or NR⁷R⁸, OR⁸, -(C₁-C₈-alkyl)-OR⁸, -(C₁-C₈-alkyl)-NR⁷R⁸ or -O₂CR⁸

where R⁷ and R⁸ are each independently C₁-C₈-alkyl, C₅-C₁₅-arylalkyl or C₄-C₁₄-aryl, or R⁷ and R⁸ together are a cyclic amino radical having a total of 4 to 20 carbon atoms,

or R¹ and R² are each independently radicals of the formula (II)



where

R⁹ is absent, or is oxygen or methylene and

R¹⁰, R¹¹ and R¹² are each independently C₁-C₁₂-alkyl, C₅-C₁₅-arylalkyl or C₄-C₁₄-aryl and

R³, R⁴, R⁵ and R⁶ are each independently R¹³, OR¹⁴ or NR¹⁵R¹⁶ where R¹³, R¹⁴, R¹⁵ and R¹⁶ are each independently C₁-C₁₂-alkyl, C₅-C₁₅-arylalkyl or C₄-C₁₄-aryl, or NR¹⁵R¹⁶ together is a cyclic amino radical having 4 to 20 carbon atoms, or R³ and R⁴ and/or R⁵ and R⁶ in each case together are -O-R¹⁷-O- where R¹⁷ is a radical selected from the group of C₂-C₄-alkylene, 1,2-phenylene, 1,3-phenylene,

1,2-cyclohexylene, 1,1'-ferrocenylene, 1,2-ferrocenylene, 2,2'-(1,1'-binaphthylene), 2,2'-(1,1')-biphenylene and 1,1'-(diphenyl-2,2'-methylene)-diyl, and the radicals mentioned may optionally be mono- or polysubstituted by radicals selected from the group of fluorine, chlorine, C₁-C₈-alkoxy and C₁-C₈-alkyl.

For the purposes of the invention, all radical definitions, parameters and illustrations mentioned hereinabove and hereinbelow, generally or in areas of preference, i.e. the particular areas and areas of preference, may be combined as desired.

DETAILED DESCRIPTION OF THE INVENTION

Alkyl, alkylene, alkoxy and alkenyl are in each case independently a straight-chain, cyclic, branched or unbranched alkyl, alkylene, alkoxy and alkenyl radical respectively. The same applies to the nonaromatic moiety of an arylalkyl radical.

C₁-C₄-Alkyl is, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl and tert-butyl, C₁-C₈-alkyl is additionally, for example, n-pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, neopentyl, 1-ethylpropyl, cyclohexyl, cyclopentyl, n-hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl, 1-ethyl-2-methylpropyl, 1-ethyl-2-methylpropyl, n-heptyl and n-octyl, C₁-C₁₂-alkyl is further additionally, for example, adamantyl, the isomeric menthyls, n-nonyl, n-decyl and n-dodecyl, and C₁-C₂₀-alkyl is still further additionally, for example, n-hexadecyl and n-octadecyl.

C₁-C₈-Alkoxy is, for example, methoxy, ethoxy, n-propoxy, isopropoxy,

n-butoxy, sec-butoxy and tert-butoxy, n-pentoxy, 1-methylbutoxy, 2-methylbutoxy, 3-methylbutoxy, neopentoxy, 1-ethylpropoxy, cyclohexoxy, cyclopentoxy, n-hexoxy and n-octoxy, and C₁-C₁₂-alkoxy is further additionally, for example, adamantoxy, the isomeric menthoxy radicals, n-decoxy and n-dodecoxy.

C₂-C₂₀-Alkenyl is, for example, vinyl, 1-propenyl, isopropenyl, 1-butenyl, 2-butenyl, 1-pentenyl, 2-pentenyl, 2-methyl-1-butenyl, 2-methyl-2-butenyl, 3-methyl-1-butenyl, 1-hexenyl, 1-heptenyl, 1-octenyl or 2-octenyl.

Fluoroalkyl is in each case independently a straight-chain, cyclic, branched or unbranched alkyl radical which is singly, multiply or fully substituted by fluorine atoms.

C₁-C₂₀-fluoroalkyl is, for example, trifluoromethyl, 2,2,2-trifluoroethyl, pentafluoroethyl, nonafluorobutyl, perfluorooctyl, perfluorododecyl and perfluorohexadecyl.

Aryl is in each case independently a heteroaromatic radical having 5 to 18 framework carbon atoms of which no, one, two or three framework carbon atoms per cycle, but at least one framework carbon atom in the entire molecule, may be substituted by heteroatoms selected from the group of nitrogen, sulphur or oxygen, but is preferably a carbocyclic aromatic radical having 6 to 18 framework carbon atoms.

Examples of carbocyclic aromatic radicals having 6 to 18 framework carbon atoms are phenyl, naphthyl, phenanthrenyl, anthracenyl or fluorenyl, and heteroaromatic radicals having 5 to 18 framework carbon atoms on which no, one, two or three framework carbon atoms per cycle, but at least one framework carbon atom in the entire molecule, may be substituted by heteroatoms selected from the group of nitrogen, sulphur or

oxygen are, for example, pyridinyl, oxazolyl, benzofuranyl, dibenzofuranyl or quinolinyl.

5 The carbocyclic aromatic radical or heteroaromatic radical may also be substituted by up to five identical or different substituents per cycle which are selected from the group of chlorine, fluorine, C₁-C₁₂-alkyl, C₁-C₁₂-fluoroalkyl, C₁-C₁₂-alkoxy, di(C₁-C₈-alkyl)amino, COO(C₁-C₈-alkyl), CON(C₁-C₈-alkyl)₂, COO(C₁-C₈-arylalkyl), COO(C₄-C₁₄-aryl), CO(C₁-C₈-alkyl), C₅-C₁₅-arylalkyl or tri(C₁-C₆-alkyl)siloxy.

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The same applies to **aryloxy** radicals.

Arylalkyl is in each case independently a straight-chain, cyclic, branched or unbranched alkyl radical which may be singly, multiply or fully substituted by aryl radicals as defined above.

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C₅-C₂₅-Arylalkyl is, for example, benzyl, diphenylbenzyl, triphenylbenzyl (trityl), 1-phenylethyl, 1-phenylpropyl, 2-phenylpropyl, 1-phenyl-1-methylethyl, 1-, 2-, 3- or 4-phenylbutyl, 1-phenyl-1-methylpropyl, 1-phenyl-2-methylpropyl, phenyl-1,1-dimethylethyl, 1-,2-,3-,4- or 5-phenylpentyl, phenyl-1-methylbutyl, phenyl-2-methylbutyl, phenyl-3-methylbutyl, phenyl-2,2-dimethylpropyl, phenyl-1-ethylpropyl, 1-naphthylmethyl, 1-naphthyl-ethyl, naphthyl-1-methylethyl, naphthylbutyl, naphthyl-1-methylpropyl, naphthyl-2-methylpropyl, naphthyl-1,1-dimethylethyl, naphthylpentyl, naphthyl-1-methylbutyl, naphthyl-2-methylbutyl, naphthyl-3-methylbutyl, naphthyl-2,2-dimethylpropyl or naphthyl-1-ethylpropyl, and also their isomeric or stereoisomeric forms.

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25

Arylalkenyl is in each case independently a straight-chain, cyclic, branched or unbranched alkenyl radical which may be singly, multiply or fully substituted by aryl radicals as defined above.

30

C₆-C₂₆-Arylalkenyl is, for example, 1-phenylvinyl or 2-phenylvinyl.

The preferred substitution patterns or compounds of the formula (I) are defined hereinbelow:

5

*¹, *², *³, *⁴ together define the following stereoisomers of the central substituted furan ring:

(1R,2R,3R,4R), (1R,2R,3R,4S), (1R,2R,3S,4S), (1R,2S,3S,4S),
10 (1R,2S,3R,4S), (1R,2S,3S,4R), (1R,2R,3S,4R), (1S,2S,3R,4S),
(1S,2S,3S,4S), (1S,2S,3S,4R), (1S,2S,3R,4R), (1S,2R,3R,4R),
(1S,2R,3S,4R), (1S,2R,3R,4S), (1S,2S,3R,4S), (1R,2R,3S,4R), preferably
(1R,2R,3R,4R), (1R,2R,3R,4S), (1R,2S,3S,4S), (1R,2S,3S,4R),
(1R,2R,3S,4R), (1S,2S,3R,4S), (1S,2S,3S,4S), (1S,2S,3S,4R),
15 (1S,2R,3R,4R), (1S,2R,3R,4S), (1S,2S,3R,4S), (1R,2R,3S,4R).

R¹ and R² are preferably each independently hydrogen, C₁-C₄-alkyl, C₄-
C₁₄-aryl, O-R⁸, O₂C-R⁸, where R⁸ is preferably C₁-C₁₂-alkyl,
C₅-C₂₅-arylalkyl or C₄-C₁₄-aryl, or OSiR¹⁰R¹¹R¹², where R¹⁰,
20 R¹¹, and R¹² are preferably each independently C₁-C₁₂-alkyl
or C₄-C₁₄-aryl.

R¹ and R² are more preferably each independently hydrogen, tert-
butoxy, trityloxy, tert-butyldimethylsilyloxy, tert-
25 butyldiphenylsilyloxy, trimethylsilyloxy, triethylsilyloxy,
triisopropylsilyloxy, neopentoxy or 1-adamantoxy.

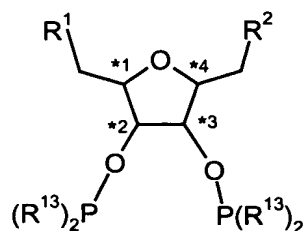
For the purposes of the invention, preference is in each case given to
those compounds of the formula (I) in which R¹ and R² are identical.

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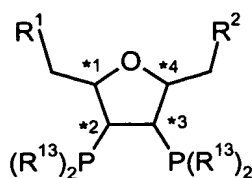
R^3 , R^4 , R^5 and R^6 are preferably each independently R^{13} , OR^{14} or $NR^{15}R^{16}$ where R^{13} , R^{14} , R^{15} and R^{16} are each independently C_1 - C_{12} -alkyl or C_4 - C_{14} -aryl, or $NR^{15}R^{16}$ together is a cyclic amino radical having 4 to 12 carbon atoms, for example pyrrolidinyl or piperidinyl, or R^3 and R^4 and/or R^5 and R^6 together are each $-O-R^{17}-O-$ where R^{17} is ethylene, 1,2-phenylene, 1,3-phenylene, 1,2-cyclohexylene, 1,1'-ferrocenylene, 1,2-ferrocenylene, di- or tetra- C_1 - C_8 -alkyl-substituted 1,1'-(diphenyl-2,2'-methylene)-diyl, 2,2'-(1,1'-binaphthylene) or 2,2'-(1,1')-biphenylene, and 2,2'-(1,1'-binaphthylene) or 2,2'-(1,1')-biphenylene is substituted at least in the 6,6'-position by radicals selected from the group of C_1 - C_8 -alkoxy and C_1 - C_8 -alkyl, and may also be substituted in the 5,5'-, 4,4'-, 3,3'- or 2,2'-position by radicals selected from the group of fluorine, chlorine, C_1 - C_8 -alkoxy and C_1 - C_8 -alkyl.

R^3 , R^4 , R^5 and R^6 are more preferably each independently R^{13} , OR^{14} or $NR^{15}R^{16}$, where R^{13} and R^{14} are each independently methyl, ethyl, n-propyl, isopropyl, tert-butyl, cyclohexyl, phenyl, 2-(C_1 - C_8)-alkylphenyl such as o-tolyl, 3-(C_1 - C_8)-alkylphenyl such as m-tolyl, 4-(C_1 - C_8)-alkylphenyl such as p-tolyl, 2,6-di-(C_1 - C_8)-alkylphenyl such as 2,6-dimethylphenyl, 2,4-di-(C_1 - C_8)-alkylphenyl such as 2,4-dimethylphenyl, 3,5-di-(C_1 - C_8)-alkylphenyl such as 3,5-dimethylphenyl, 3,4,5-tri-(C_1 - C_8)-alkylphenyl such as mesityl and isityl, 2-(C_1 - C_8)-alkoxyphenyl such as o-anisyl and o-phenetyl, 3-(C_1 - C_8)-alkoxyphenyl such as m-anisyl and m-phenetyl, 4-(C_1 - C_8)-alkoxyphenyl such as p-anisyl and p-phenetyl, 2,4-di-(C_1 - C_8)-alkoxyphenyl such as 2,4-dimethoxyphenyl, 2,6-di-(C_1 - C_8)-alkoxyphenyl such as 2,6-dimethoxyphenyl, 3,5-di-(C_1 - C_8)-alkoxyphenyl such as 3,5-dimethoxyphenyl, 3,4,5-tri-(C_1 - C_8)-alkoxyphenyl such as 3,4,5-trimethoxyphenyl, 3,5-dialkyl-4-(C_1 - C_8)-alkoxyphenyl such as 3,5-dimethyl-4-anisyl, 3,5-(C_1 - C_8)-dialkyl-4-di-

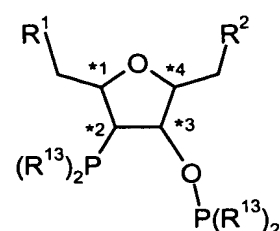
- (C₁-C₈)-alkylaminophenyl, 3,5-dimethyl-4-dimethylamino-phenyl, 4-di-(C₁-C₈)-alkylaminophenyl such as 4-diethylaminophenyl and 4-dimethylaminophenyl, 3,5-bis-[(C₁-C₄)-fluoroalkyl]phenyl such as 3,5-bis-trifluoromethylphenyl, 2,4-bis-[(C₁-C₄)-fluoroalkyl]phenyl such as 2,4-bis-trifluoromethylphenyl, 4-[(C₁-C₄)-fluoroalkyl]phenyl such as 4-trifluoromethylphenyl and mono-, di-, tri-, tetra- or penta-fluorine- and/or -chlorine-substituted phenyl, fluorenyl or naphthyl, such as 4-fluorophenyl and 4-chlorophenyl, or NR¹⁵R¹⁶ as a whole is dimethylamino, diethylamino, pyrrolidino or diisopropylamino. R³ and R⁴ and/or R⁵ and R⁶, each in pairs, are also more preferably O-R¹⁷-O where R¹⁷ is 1,1'-bis-(4,6-di-(C₁-C₈-alkyl)-phenyl)-2,2'-methylene-diyl, in particular 1,1'-bis-(4-methyl-6-tert-butylphenyl)-2,2'-methylene-diyl and 1,1'-bis-(4-methyl-6-(1-methylcyclohexyl)-phenyl)-2,2'-methylene-diyl, or where R¹⁷ is (R)-1,1'-biphenyl-2,2'-diyl, (S)-1,1'-biphenyl-2,2'-diyl, (R)-1,1'-binaphthyl-2,2'-diyl, (S)-1,1'-binaphthyl-2,2'-diyl, 1,1'-[bis-(4-methyl-6-tert-butylphenyl)-2,2'-methylene]]-diyl or 1,1'-[bis-(4-methyl-6-(1-methylcyclohexyl)-2,2'-methylene)]-diyl.
- For the purposes of the invention, preference is given in each case to those compounds of the formula (I) in which R³ and R⁴ and/or R⁵ and R⁶ in pairs are identical.
- Particularly preferred compounds of the formula (I) are those of the formulae (Ia) to (Ii)



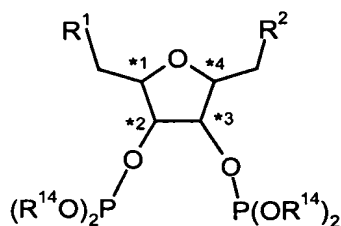
(Ia)



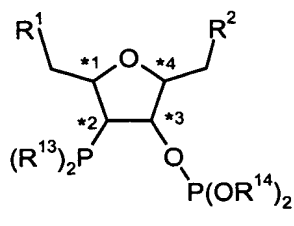
(Ib)



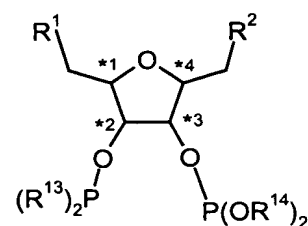
(Ic)



(Id)

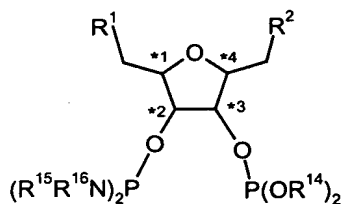


(Ie)

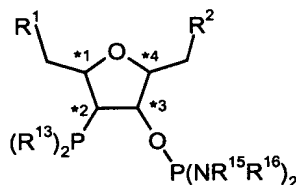


(If)

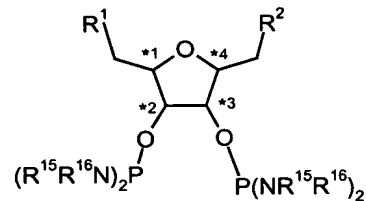
5



(Ig)



(Ih)



(Ii)

where *1, *2, *3, *4, R¹, R², R¹³, R¹⁴, R¹⁵ and R¹⁶ each have the definition and areas of preference specified under formula (I).

10

Compounds of the formula (I) include:

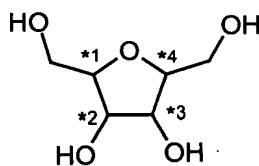
2,3-bis-O-(diphenylphosphino)-1,6-di-O-(triphenylmethyl)-2,5-anhydro-D-mannitol, 2,3-bis-O-(diphenylphosphino)-1,6-dideoxy-2,5-anhydro-D-mannitol, 2,3-bis-O-(diphenylphosphino)-1,6-di-O-(*tert*-butyldiphenylsilyl)-2,5-anhydro-D-mannitol, 2,3-bis-O-(diphenylphosphino)-1,6-di-O-(triphenylmethyl)-2,5-anhydro-L-iditol, 2,3-bis-O-(diphenylphosphino)-1,6-di-O-(*tert*-butyldiphenylsilyl)-2,5-anhydro-L-iditol, 2,3-bis-O-

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(diphenylphosphino)-1,6-dideoxy-2,5-anhydro-L-iditol, 2,3-bis-O-(di(4-methoxyphenyl)phosphino)-1,6-di-O-(*tert*-butyldiphenylsilyl)-2,5-anhydro-D-mannitol, 2,3-bis-O-(di((4-Trifluoromethyl)phenyl)phosphino)-1,6-di-O-(*tert*-butyldiphenylsilyl)-2,5-anhydro-D-mannitol, 2-O-(di(2,4-dimethylphenyl)phosphino)-3-O-(diphenylphosphino)-1,6-di-O-(*tert*-butyldiphenylsilyl)-2,5-anhydro-D-mannitol, 2-O-(di(2,4-dimethylphenyl)phosphino)-3-O-(4,8-ditert-butyl-2,10-dimethyl-12H-dibenzo[δ,γ][1,3,2]dioxaphosphocino)-1,6-di-O-(*tert*-butyldiphenylsilyl)-2,5-anhydro-D-mannitol and 2-O-(di(2,4-dimethylphenyl)phosphino)-3-O-(2,10-dimethyl-4,8-bis(1-methylcyclohexyl)-12H-dibenzo[δ,γ]-[1,3,2]dioxaphosphocino)-1,6-di-O-(*tert*-butyldiphenylsilyl)-2,5-anhydro-D-mannitol.

For the purposes of the invention, the term stereoisomerically enriched includes in particular stereoisomerically pure compounds or else mixtures of stereoisomeric compounds in which one stereoisomer is present in a larger relative proportion than the other stereoisomer or stereoisomers, preferably in a relative proportion of 50 to 100 mol%, more preferably 90 to 100 mol% and most preferably 98 to 100 mol%.

The compounds of the formula (I) and (Ia) to (Ii) can be prepared starting from the known 2,5-anhydrocyclopentoses of the formula (III).



(III)

2,5-anhydrocyclopentoses of the formula (III) are, for example: 2,5-anhydro-D-mannitol, 2,5-anhydro-L-mannitol, 2,5-anhydro-L-iditol, 2,5-anhydro-D-iditol, 2,5-anhydro-L-glucitol, 2,5-anhydro-D-glucitol, 2,5-

anhydro-altritol, 2,5-anhydro-D-altritol, 2,5-anhydro-galactitol, 2,5-anhydro-allitol.

Preferred compounds of the general formula (III) are:

5 2,5-anhydro-D-mannitol and 2,5-anhydro-L-iditol. For the purposes of the present invention, preference is given in particular to those compounds of the formula (I) which are obtainable starting from 2,5-anhydro-D-mannitol and 2,5-anhydro-L-iditol by the methods described hereinbelow.

10 The compounds of the formula (III) can be converted by reacting with compounds of the formula (IV)



15 where

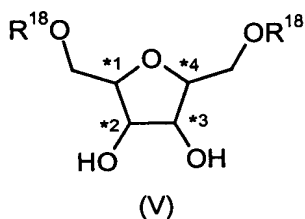
R^{18} is R^8 , $R^8\text{CO}$ or $\text{OSiR}^{10}\text{R}^{11}\text{R}^{12}$ and where R^8 , R^{10} , R^{11} and R^{12} each have the definition and areas of preference specified under (I) or R^{18} is $R^{19}\text{-SO}_2\text{-}$ where R^{19} is $\text{C}_1\text{-C}_{12}\text{-alkyl}$, $\text{C}_1\text{-C}_{12}\text{-fluoroalkyl}$, $\text{C}_5\text{-C}_{25}\text{-arylalkyl}$ or

20 $\text{C}_4\text{-C}_{24}\text{-aryl}$ and

Hal is chlorine, bromine or iodine

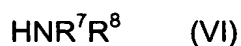
to compounds of the formula (V)

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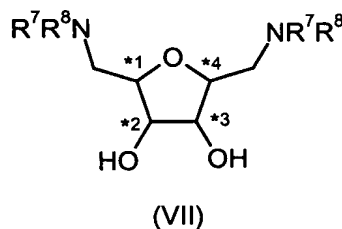
where R^{18} is in each case independently as defined under formula (IV).

Compounds of the formula (V) where R^{18} is $R^{19}SO_2^-$ can also be converted by reacting with amines of the formula (VI)



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where R^7 and R^8 each independently have the definitions and areas of preference specified under formula (I) to compounds of the formula (VII)



10 where R^7 and R^8 are each independently as defined under formula (IV).

Compounds of the formula (V) in which R^{18} is $R^{19}SO_2^-$ can also be converted by reacting with complex hydrides of the formula (VIII)



15

where Met^1 is lithium, sodium or potassium, preferably lithium,

R^{20} is hydrogen

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n is 1, 2, 3 or 4, preferably 4 and

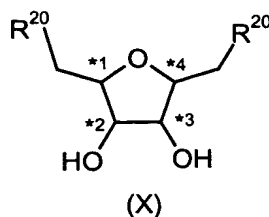
R^{20} is C_1 - C_4 -alkyl,

25

or by reacting organolithium compounds of the formula (IX)



where R^{20} is C_1 - C_{20} -alkyl, C_1 - C_{20} -fluoroalkyl, C_2 - C_{20} -alkenyl, C_4 - C_{24} -aryl, C_5 - C_{25} -arylalkyl, C_6 - C_{26} -arylalkenyl, $-(C_1-C_8\text{-alkyl})-OR^8$, $-(C_1-C_8\text{-alkyl})-$
 5 NR^7R^8 or protected (for example as a cyclic acetal) $-(C_1-C_8\text{-alkyl})-CO-R^8$
 to compounds of the formula (X)

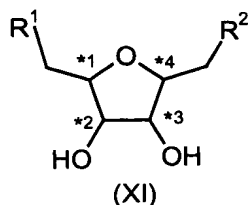


10 where R^{20} is as defined under formulae (VIII) and (IX).

As a consequence of the acidity of the free 2- and 3-hydroxyl groups, it is advantageous to use an excess of the organolithium compounds or of the complex hydrides or to protect the 3,4-diol unit in a manner known per se
 15 by conversion, for example, to a cyclic acetal, and subsequently deprotecting it again.

The compounds of the formulae (V), (VII) and (X) together are encompassed by the compounds of the formula (XI), which can be used
 20 as intermediates for preparing the compounds of the formula (I) according to the invention.

In formula (XI)



R^1 and R^2 each have the same definition and areas of preference as described under formula (I).

5 The compounds of the formula (XI) can be used in a manner known in principle (see also Rajan Babu, J. Org. Chem., 1997, 62, 6012-6028), by reacting with compounds of the formula (XIIa)

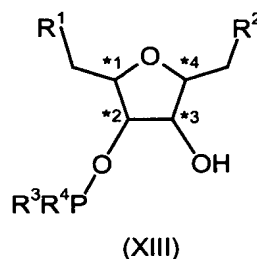


10 where R^3 and R^4 each have the same definition and areas of preference as specified under formula (I) and

Y is chlorine, bromine, iodine, dimethylamino or diethylamino, preferably chlorine,

15

to obtain the compounds of the formula (XIII)



20 where R^1 , R^2 , R^3 and R^4 each have the same definition and areas of preference as described under formula (I).

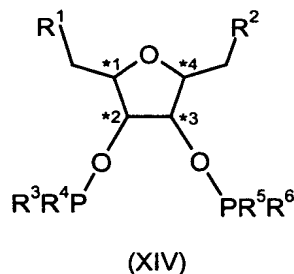
The compounds of the formula (XIII) can also be reacted with compounds of the formula (XIIb)

25



where R^5 and R^6 each have the same definitions and areas of preference as specified under formula (I) and Y has the same definition and areas of preference as specified under formula (XIIa)

5 to give compounds of the formula (XIV)



10 where R^1 , R^2 , R^3 , R^4 , R^5 and R^6 each have the same definitions and areas of preference as specified under formula (I).

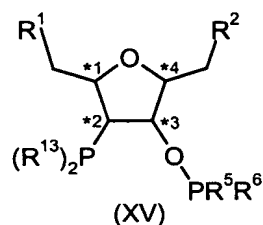
15 When compound (XIIa) and (XIIb) are identical, the reaction can also be carried out in one step. Advantageously, the conversions of (XI) to (XIV), (XI) to (XIII) or (XIII) to (XIV) are carried out in the presence of a base, for example amines or aromatic nitrogen bases such as triethylamine, pyridine or 4-dimethylaminopyridine. Alternatively, the conversion can also be effected after at least partial deprotonation of the alcohol functions.

20 Examples of suitable solvents for the conversions are chlorinated alkanes such as methyl chloride, alkylic hydrocarbons, e.g. hexane, cyclohexane, aromatic hydrocarbons, e.g. toluene, pyridines, benzene, ketones, e.g. acetone, or carboxylic esters, e.g. ethyl acetate, or dialkyl ethers, e.g. THF or MTBE. The solvent used is preferably methylene chloride.

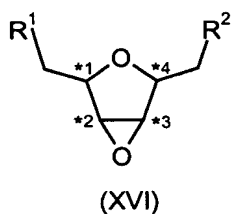
25 In the manner described, the compounds of the formulae (Ia), (Id), (If), (Ig) and (Ii) in particular with the above-specified definition and areas of preference are obtainable.

The compounds of the formulae (XIII) and (XIV) are likewise encompassed by the invention. The same definitions and areas of preference apply as specified under formula (I).

5 Compounds of the formula (XV)



10 where R^1 , R^2 , R^5 , R^6 and R^{13} each have the definitions and areas of preference specified under formula (I) can also be prepared by a process according to the invention by converting compounds of the formula (XVI)



15 where R^1 and R^2 have the definition and areas of preference specified under formula (I), in the presence of compounds of the formula (XVII)



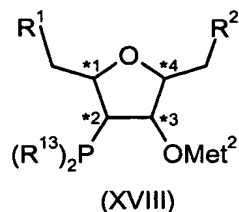
20 where

Met^2 is lithium, sodium or potassium and

R^{13} has the definition and areas of preference specified under formula (I)

to compounds of the formula (XVIII)

5

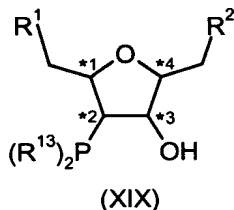


where R^1 , R^2 , Met^2 and R^{13} are each as defined above,

10 and reacting the compounds of the formula (XVIII) with compounds of the formula (XIb) as defined there to give compounds of the formula (XV).

Alternatively, the compounds of the formula (XVII) can be converted by acidifying to compounds of the formula (XIX)

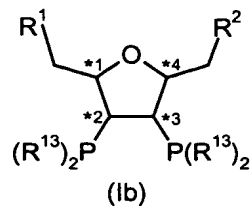
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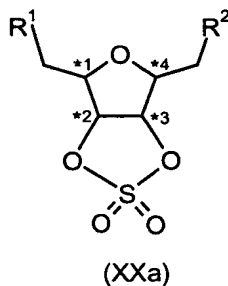
and then converted by reacting with compounds of the formula (XIb) to compounds of the formula (XV). This reaction can be carried out as
20 described for the preparation of the compounds of the formula (XIV).

The compounds of the formula (XV) include in particular the compounds of the formulae (Ic), (Ie), (If) and (Ih) preferred according to the invention.

The compounds of the formula (Ib)

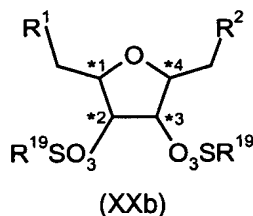


- 5 can be prepared, for example, in a manner known per se (see also Terfort, Synthesis, 1992, 951-953) by reacting compounds of the formula (XXa)

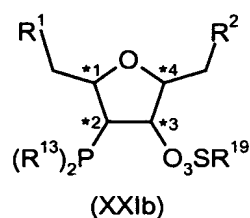
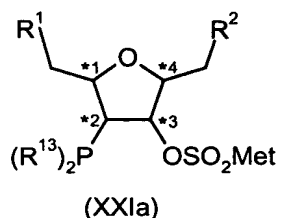


10

or compounds of the formula (XXb)



- 15 where R¹ and R² have the definition and areas of preference specified under formula (I) and R¹⁹ has the definition and areas of preference specified under formula (VII) initially with phosphides of the formula (XVII), thus obtaining compounds of the formula (XXIa) or compounds of the formula (XXIb)



and reacting the compounds of the formula (XXIa) or compounds of the
 5 formula (XXIb) with compounds of the formula (XVII) to give compounds
 of the formula (Ib).

When the radicals $P(R^{13})_2$ in formula (Ib) are identical, the conversion can
 also be effected in one step.

10

The compounds of the formulae (XXIa) and (XXIb) are likewise
 encompassed by the invention.

Some of the compounds of the formula (XXb) are known from the
 15 literature (see, for example, Tetrahedron: Asymmetry, 2000, 11, 2899 to
 2906). Further compounds of the formulae (XXa) and (XXb) can be
 prepared in a similar manner to the literature. The compounds of the
 formula (XXb) are likewise encompassed by the invention as particularly
 suitable intermediate compounds for preparing compounds of the formula
 20 (I).

The invention also encompasses transition metal complexes which
 contain the compounds of the formula (I) according to the invention.

25 Transition metal complexes are preferably those of ruthenium, osmium,
 cobalt, rhodium, iridium, nickel, palladium, platinum and copper, preferably
 those of ruthenium, rhodium, iridium, nickel, palladium, platinum and
 copper.

The transition metal complexes according to the invention are suitable in particular as catalysts. The invention therefore also encompasses catalysts which contain the transition metal complexes according to the invention.

5

Useful catalysts are, for example, either isolated transition metal complexes or those transition metal complexes which are obtainable by reacting transition metal compounds and compounds of the formula (I).

10 Isolated transition metal complexes which contain the compounds of the formula (I) are preferably those in which the ratio of transition metal to compound of the formula (I) is 1:1.

15 Preference is given to the compounds according to the invention of the formula (XXIII)



20 where (I) is a compound of the formula (I) with the definition and areas of preference specified there and

M is rhodium or iridium and

25 L^1 is in each case a C_2 - C_{12} -alkene, for example ethylene or cyclooctene, or a nitrile, for example acetonitrile or benzonitrile or benzyl nitrile, or

L^1_2 together is a (C_4 - C_{12})-diene, for example bicyclo[2.1.1]hepta-2,5-diene (norbornadiene) or 1,5-cyclooctadiene.

30

Compounds of the formula (XXIII) include:

[Rh(cod)(2,3-bis-O-(diphenylphosphino)-1,6-di-O-(triphenylmethyl)-2,5-anhydro-D-mannitol)]BF₄, [Rh(cod)(2,3-bis-O-(diphenylphosphino)-1,6-di-O-(*tert*-butyldiphenylsilyl)-2,5-anhydro-D-mannitol)]BF₄, [Rh(cod)(2,3-bis-O-(diphenylphosphino)-1,6-dideoxy-2,5-anhydro-D-mannitol)]BF₄ and
 5 [Ir(cod)(2,3-bis-O-(diphenylphosphino)-1,6-di-O-(*tert*-butyldiphenylsilyl)-2,5-anhydro-D-mannitol)]BF₄.

Preferred transition metal complexes are those which are obtainable by reacting transition metal compounds and compounds of the formula (I).

10

Suitable transition metal compounds are, for example, those of the formula (XXIIa)



15

where

M is rhodium, iridium, ruthenium, nickel, palladium, platinum or copper and

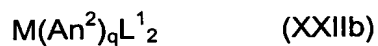
20

An¹ is chloride, bromide, acetate, nitrate, methanesulphonate, trifluoromethanesulphonate or acetylacetonate and

q is 3 for rhodium, iridium and ruthenium, is 2 for nickel, palladium and platinum, and is 1 for copper,

25

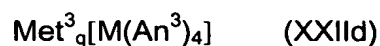
or transition metal compounds of the formula (XXIIb),



30

where

- M is ruthenium, iridium, ruthenium, nickel, palladium, platinum or copper and
- 5 An² is chloride, bromide, acetate, methanesulphonate or trifluoro-methanesulphonate, tetrafluoroborate or hexafluorophosphate, perchlorate, hexafluoroantimonate, tetra(bis-3,5-trifluoromethylphenyl)-borate or tetraphenylborate and
- 10 q is 1 for rhodium and iridium, is 2 for ruthenium, nickel, palladium and platinum, and is 1 for copper,
- 15 L¹ is in each case a C₂-C₁₂-alkene, for example ethylene or cyclooctene, or a nitrile, for example acetonitrile, benzonitrile or benzyl nitrile, or
- L¹₂ together is a (C₄-C₁₂)-diene, for example bicyclo[2.1.1]hepta-2,5-diene (norbornadiene) or 1,5-cyclooctadiene,
- or transition metal compounds of the formula (XXIIc)
- 20
$$[ML^2An^1_2]_2 \quad (XXIIc)$$
- where
- 25 M is ruthenium and
- L² is an aryl radical, for example cymene, mesityl, phenyl or cyclooctadiene, norbornadiene or methylallyl
- 30 or transition metal compounds of the formula (XXIId),



where

5 M is palladium, nickel, iridium or rhodium and

An^3 is chloride or bromide and

10 Met^3 is lithium, sodium, potassium, ammonium or organic ammonium
and

 q is 3 for rhodium and iridium, and is 2 for nickel, palladium and
platinum,

15 or transition metal compounds of the formula (XXIle),



where

20 M is iridium or rhodium and

L^3 is ($\text{C}_4\text{-C}_{12}$)-diene, for example bicyclo[2.1.1]hepta-2,5-diene
(norbornadiene) or 1,5-cyclooctadiene and

25 An^4 is a noncoordinating or weakly coordinating anion, for example
methanesulphonate, trifluoromethanesulphonate, tetrafluoroborate,
hexafluorophosphate, perchlorate, hexafluoroantimonate, tetra(bis-
3,5-trifluoromethylphenyl)-borate or tetraphenylborate.

30 Also suitable as transition metal compounds are, for example, Ni(1,5-
cyclooctadiene)₂, Pd₂(dibenzylideneacetone)₃, Pd[PPh₃]₄,

cyclopentadienyl₂Ru, Rh(acac)(CO)₂, Ir(pyridine)₂(1,5-cyclooctadiene), Cu(phenyl)Br, Cu(phenyl)Cl, Cu(phenyl)I, Cu(PPh₃)₂Br, [Cu(CH₃CN)₄]BF₄ and [Cu(CH₃CN)₄]PF₆ or multinuclear bridged complexes, for example [Rh(1,5-cyclooctadiene)Cl]₂, [Rh(1,5-cyclooctadiene)Br]₂,

5 [Rh(ethene)₂Cl]₂ or [Rh(cyclooctene)₂Cl]₂.

The transition metal compounds used are preferably:

[Rh(cod)Cl]₂, [Rh(cod)Br]₂, [Rh(cod)₂]ClO₄, [Rh(cod)₂]BF₄, [Rh(cod)₂]PF₄, [Rh(cod)₂]ClO₆, [Rh(cod)₂]OTf, [Rh(cod)₂]BAr₄ (Ar = 3,5-bistrifluoromethylphenyl), [Rh(cod)₂]SbF₆, RuCl₂(cod), [(cymene)RuCl₂]₂, [(benzene)-
10 RuCl₂]₂, [(mesityl)RuCl₂]₂, [(cymene)RuBr₂]₂, [(cymene)RuI₂]₂, [(cymene)-Ru(BF₄)₂]₂, [(cymene)Ru(PF₆)₂]₂, [(cymene)Ru(BAr₄)₂]₂ (Ar = 3,5-bistrifluoromethylphenyl), [(cymene)Ru(SbF₆)₂]₂, [Ir(cod)Cl]₂, [Ir(cod)₂]PF₆, [Ir(cod)₂]ClO₄, [Ir(cod)₂]SbF₆, [Ir(cod)₂]BF₄, [Ir(cod)₂]OTf, [Ir(cod)₂]BAr₄
15 (Ar = 3,5-bistrifluoromethylphenyl), RuCl₃, NiCl₃, RhCl₃, PdCl₂, PdBr₂, Pd(OAc)₂, Pd₂(dibenzylideneacetone)₃, Pd(acetyl-acetonate)₂, CuOTf, CuI, CuCl, Cu(OTf)₂, CuBr, CuI, CuBr₂, CuCl₂, CuI₂, [Rh(nbd)Cl]₂, [Rh(nbd)Br]₂, [Rh(nbd)₂]ClO₄, [Rh(nbd)₂]BF₄, [Rh(nbd)₂]PF₆, [Rh(nbd)₂]OTf, [Rh(nbd)₂]BAr₄ (Ar = 3,5-bistrifluoro-methylphenyl),
20 [Rh(nbd)₂]SbF₆, RuCl₂(nbd), [Ir(nbd)₂]PF₆, [Ir(nbd)₂]ClO₄, [Ir(nbd)₂]SbF₆, [Ir(nbd)₂]BF₄, [Ir(nbd)₂]OTf, [Ir(nbd)₂]BAr₄ (Ar = 3,5-bistrifluoromethylphenyl), Ir(pyridine)₂(nbd), [Ru(DMSO)₄Cl₂], [Ru(CH₃CN)₄Cl₂], [Ru(PhCN)₄Cl₂], [Ru(cod)Cl₂]_n, [Ru(cod)₄(methallyl)₂], [Ru(acetylacetonate)₃].

25 Still greater preference is given to [Rh(cod)Cl]₂, [Rh(cod)Br]₂, [Rh(cod)₂]ClO₄, [Rh(cod)₂]BF₄, [Rh(cod)₂]PF₄, [Rh(cod)₂]ClO₆, [Rh(cod)₂]OTf, [Rh(cod)₂]BAr₄ (Ar = 3,5-bistrifluoromethylphenyl), [Rh(cod)₂]SbF₆, [Rh(nbd)Cl]₂, [Rh(nbd)Br]₂, [Rh(nbd)₂]ClO₄, [Rh(nbd)₂]BF₄, [Rh(nbd)₂]PF₆, [Rh(nbd)₂]OTf, [Rh(nbd)₂]BAr₄ (Ar = 3,5-bistrifluoromethylphenyl), [Rh(nbd)₂]SbF₆, [Ir(cod)Cl]₂, [Ir(cod)₂]PF₆,

30

$[\text{Ir}(\text{cod})_2]\text{ClO}_4$, $[\text{Ir}(\text{cod})_2]\text{SbF}_6$, $[\text{Ir}(\text{cod})_2]\text{BF}_4$, $[\text{Ir}(\text{cod})_2]\text{OTf}$, $[\text{Ir}(\text{cod})_2]\text{BAr}_4$
(Ar = 3,5-bis(trifluoromethyl)phenyl).

5 The amount of the transition metal compounds used may, for example, be 25 to 200 mol%, based on the chiral diphosphorus compound of the general formula (I) used, preferably 50 to 150 mol%, very particularly preferably 75 to 125 mol% and even more preferably 100 to 115 mol%.

10 The catalysts which contain the transition metal complexes according to the invention are suitable in particular for use in a process for preparing stereoisomerically enriched, preferably enantiomerically enriched, compounds.

15 Preference is given to using the catalysts for asymmetric 1,4-additions, asymmetric hydroformylations, asymmetric hydrocyanations, asymmetric Heck reactions and asymmetric hydrogenations, more preferably for asymmetric hydrogenations.

20 Preferred asymmetric hydrogenations are, for example, hydrogenations of prochiral C=C bonds for example prochiral enamines, olefins, enol ethers, C=O bonds, for example prochiral ketones, and C=N bonds, for example prochiral imines. Particularly preferred asymmetric hydrogenations are hydrogenations of prochiral C=C bonds, for example prochiral enamines, olefins, and C=N bonds, for example prochiral imines.

25 The invention therefore also encompasses a process for preparing stereoisomerically enriched, preferably enantiomerically enriched, compounds by catalytic hydrogenation of olefins, enamines, enamides, imines or ketones, which is characterized in that the catalysts used are
30 those which contain the transition metal complexes of compounds of the formula (I) as defined there.

The amount of the transition metal compound or of the transition metal complex used may, for example, be 0.001 to 5 mol%, based on the substrate used, preferably 0.001 to 0.5 mol%, very particularly preferably 0.001 to 0.1 mol% and even more preferably 0.001 to 0.008 mol% .

5

In a preferred embodiment, asymmetric hydrogenations can be carried out, for example, in such a manner that the catalyst is obtained for a transition metal compound and compound of the formula (I), optionally in a suitable solvent, the substrate is added and the reaction mixture is placed

10

under hydrogen pressure at room temperature.

The metal compounds used for asymmetric hydrogenations are particularly preferably those of the general formula (XXIV)

15



where M is rhodium or iridium, and L^3 and An are as defined above,

or dinuclear complexes, for example $[Rh(1,5\text{-cyclooctadiene})Cl]_2$, $[Rh(1,5\text{-cyclooctadiene})Br]_2$, $[Rh(ethene)_2Cl]_2$, $[Rh(cyclooctene)_2Cl]_2$.

20

Particularly preferred metal compounds for asymmetric hydrogenations are $[Rh(cod)_2]OTf$, $[Rh(cod)_2]BF_4$, $[Rh(cod)_2]PF_6$, $[Rh(nbd)_2]PF_6$, $[Rh(nbd)_2]BF_4$, and $[Rh(norbornadiene)_2]OTf$, $[Ir(cod)_2]BF_4$ and $[Ir(cod)_2]PF_6$.

25

In a particularly preferred embodiment, transition metal compound and compound of the formula (I) are dissolved in degassed solvent in a baked-out glass autoclave. The mixture is stirred for approx. 5 min and the substrate is subsequently added in degassed solvent. After setting a

30

particular temperature, hydrogenation is effected under elevated H₂ pressure.

5 Suitable solvents for asymmetric catalysis are, for example, chlorinated alkanes such as methyl chloride, short-chain C₁-C₆-alcohols, e.g. methanol, isopropanol or ethanol, aromatic hydrocarbons, e.g. toluene or benzene, ketones, e.g. acetone, or carboxylic esters, e.g. ethyl acetate.

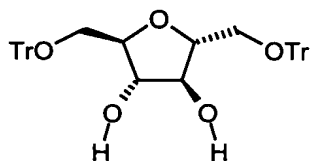
10 The asymmetric catalysis is advantageously carried out at a temperature of -20°C to 200°C, preferably 0 to 100°C and more preferably 20° to 70°C.

The hydrogen pressure may, for example, be 0.1 to 200 bar, preferably 0.5 to 100 bar and more preferably 1 to 70 bar.

15 The catalysts according to the invention are suitable in particular in a process for preparing stereoisomerically enriched, preferably enantiomerically enriched, active ingredients in pharmaceuticals and agrochemicals, or intermediates of these two classes.

20 The advantage of the present invention is that the ligands can be prepared in an efficient manner and their electronic and steric properties are variable to a high degree starting from readily available reactants. The ligands according to the invention and their transition metal complexes, especially in asymmetric hydrogenations of C=C bonds and imines, also
25 exhibit turnover frequencies (TOFs) of over 1000/h, which are well above those of comparable systems.

The invention is further illustrated but is not intended to be limited by the following examples in which all parts and percentages are by weight
30 unless otherwise specified.

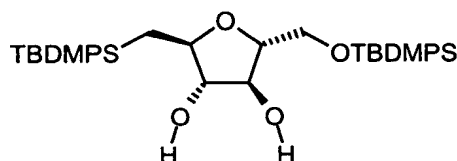
EXAMPLES**Example 1:**

5

1,6-Di-O-(triphenylmethyl)-2,5-anhydro-D-mannitol (B1): a mixture of 2.35 g (14.33 mmol) of 2,5-anhydro-D-mannitol and 8.79 g (31.53 mmol) of triphenylmethyl chloride in 38 ml of pyridine was stirred at 100°C for 12 hours. After cooling, the mixture was diluted with CH₂Cl₂, and washed with aq.HCl (0.78 mol/l), the organic phase was dried over Na₂SO₄ and the solvent was subsequently removed under reduced pressure. The crude product was purified by means of column chromatography (hexane/ethyl acetate 2:1). Yield: 5.57 g (60% of theory).

¹H NMR (400 MHz, CHCl₃) δ, 7.60-7.03 (m, 15H, Ph), 4.12 (m, 1H, H-2), 3.96 (m, 1H, H-3), 3.45 (dd, 1H, J_{6,2}= 3.9 Hz, J_{6,6'}=10.2 Hz, H-6), 3.39 (sa, 1H, OH), 3.22 (dd, 1H, J_{6',2}= 4.2 Hz, J_{6',6}=10.2 Hz, H-6'); ¹³C NMR (100.6 MHz) δ, 143.31.-127.02 (Ph), 87.31 (C(Ph)₃), 83.63 (C-2), 79.45 (C-3), 64.79 (C-6).

20

Example 2:

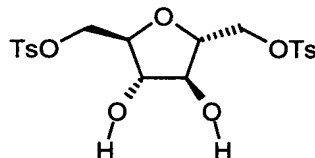
1,6-Di-O-(*tert*-butyldiphenylsilyl)-2,5-anhydro-D-mannitol (B2): 3 ml (11.66 mmol) of *tert*-butyldiphenylsilyl chloride (TBDMPSCI) were added

25

dropwise at 0°C to a solution of 0.87 g (5.3 mmol) of 2,5-anhydro-D-mannitol and 1.5 g (22.28 mmol) of imidazole in 12 ml of anhydrous DMF. The mixture was heated to room temperature and stirred for a further 25 hours, and the solvent was subsequently removed under reduced pressure. The mixture was diluted with CH₂Cl₂ and washed with water, the organic phase was dried over Na₂SO₄ and the solvent was subsequently removed under reduced pressure. The crude product was purified by means of column chromatography (hexane/ethyl acetate 4:1). Yield 1.36 g (40% of theory).

¹H NMR (400 MHz, CDCl₃) δ, 7.81-7.30 (m, 10H, Ph); 4.25 (m, 1H, H-3); 4.17 (m, 1H, H-2); 4.04 (d, 1H, OH); 3.86 (dd, 1H, J_{6,2}= 3.7 Hz, J_{6,6'}=11.1 Hz, H-6); 3.75 (dd, 1H, J_{6',2}= 3.2 Hz, J_{6,6'}=11.1 Hz, H-6'); 1.07 (s, 9H, C(CH₃)₃); ¹³C NMR (100.6 MHz) δ, 136.10-126.99 (Ph), 87.09 (C-2), 79.71 (C-3), 65.52 (C-6), 26.73 (C(CH₃)₃), 19.02 (C(CH₃)₃).

Example 3:



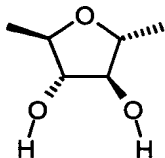
1,6-Di-O-(*p*-toluenesulphonyl)-2,5-anhydro-D-mannitol (B3): 5.33 g (27.945 mmol) of *p*-toluenesulphonyl chloride were added at 0°C to a solution of 2.16 g (13.15 mmol) of 2,5-anhydro-D-mannitol in 88 ml of pyridine. The mixture was heated to room temperature and stirred for a further 24 hours. The reaction was hydrolysed using ice-water and extracted using CH₂Cl₂, and the combined organic phases were washed with 3N HCl and NaCl. After drying over MgSO₄, the solvent was subsequently removed under reduced pressure. The crude product was

purified by means of column chromatography (hexane/ethyl acetate 1:2).

Yield: 3.00 g (48% of theory).

¹H NMR (400 MHz, CDCl₃) δ, 7.82-7.31 (m, 4H, Ph); 4.2-3.9 (m, 4H, H-2, H-3, H-6, H-6'); 2.44 (s, 3H, CH₃); ¹³C NMR (100.6 MHz, CDCl₃) δ, 145.05-126.86 (Ph), 80.42 (C-2), 77.32 (C-3), 68.84 (C-6), 21.81 (CH₃).

Example 4:



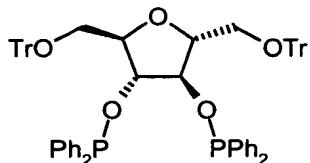
10

1,6-Dideoxy-2,5-anhydro-D-mannitol (B4): 0.86 g (22.66 mmol) of LiAlH₄ was added to a solution of 3.60 g (7.63 mmol) of **B3** in 20 ml of anhydrous THF and stirred at reflux for 2 hours. After cooling, Arberlite® IR-120(plus) was added and stirring was continued until hydrogen evolution had ended.

15 The mixture was filtered through Celite® and the solvent was subsequently removed under reduced pressure. The crude product was purified by means of column chromatography (CH₂Cl₂ / MeOH= 12:1). Yield: 0.84 g (84% of theory).

20 ¹H NMR (400 MHz, CDCl₃) δ, 3.84 (m, 1H, H-2), 3.64 (m, 1H, H-3), 1.27 (d, 1H, J_{6,2}= 6 Hz, H-6); ¹³C NMR (100.6 MHz; CDCl₃) δ, 84.18 (C-2), 79.29 (C-3), 19.61 (C-6).

Example 5:

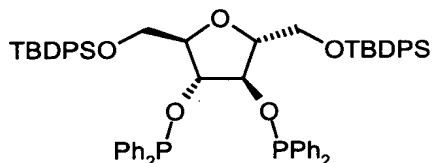


25

2,3-bis-O-(Diphenylphosphino)-1,6-di-O-(triphenylmethyl)-2,5-anhydro-D-mannitol (B5). 0.61 ml (4.4 mmol) of anhydrous Et₃N was added to a solution of 0.63 g (1.0 mmol) of **B1** in 5 ml of anhydrous, degassed CH₂Cl₂. At -15°C, a solution of 0.39 ml (2.2 mmol) of diphenylchlorophosphine in 3 ml of CH₂Cl₂ was slowly added dropwise. After stirring at -15°C for 15 minutes, ethyl ether was added, the salts were filtered off through Celite® and the solvent was subsequently removed under reduced pressure. The crude product was purified by means of column chromatography under argon (hexane / ethyl acetate 15:1). Yield 0.51 g (51% of theory).

[α]_D = + 0.4 (c 1.04, CHCl₃); ¹H NMR (400 MHz, CHCl₃) δ, 7.60-7.02 (m, 25H, Ph), 4.62 (m, 1H, H-3), 4.29 (m, 1H, H-2), 3.198 (d, 2H, J_{6,2} = 5.6 Hz, H-6, H-6'); ¹³C NMR (100.6 MHz) δ, 144.33-127.06 (Ph), 86.901 (C(Ph)₃), 86.14 (m, C-3), 83.51 (m, C-2), 64.25 (s, C-6); ³¹P NMR (161.974 MHz, CDCl₃) δ, 116.23 (s). Anal calcd for C₆₈H₅₈O₅P₂: C, 80.29; H, 5.74; found C, 79.99; H, 5.72.

Example 6:

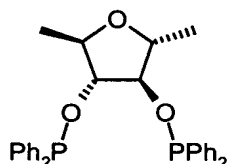


2,3-bis-O-(Diphenylphosphino)-1,6-di-O-(tert-butyldiphenylsilyl)-2,5-anhydro-D-mannitol (B6): This product was prepared from **B2** at -25°C in a similar manner to Example 5. Yield: 0.816 g (50%), white oil.

[α]_D = + 9.9 (c 1.8, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ, 7.81-7.02 (m, 20H, Ph), 4.88 (m, 1H, H-3), 4.18 (m, 1H, H-2), 3.76 (dd, 1H, JH-6), 3.63

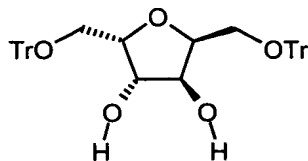
(d, 1H, H-6'); 1.02 (s, 9H, C(CH₃)₃); ¹³C NMR (100.6 MHz, CDCl₃) δ, 144.02-126.10 (Ph), 86.14 (m, C-3), 83.51 (m, C-2), 64.25 (s, C-6), 26.79 (C(CH₃)₃), 19.26 (C(CH₃)₃); ³¹P NMR (161.974 MHz, CDCl₃) δ, 116.23 (s). Anal calcd for C₆₂H₆₆O₅P₂Si₂: C, 73.78; H, 6.59; found C, 73.65; H, 6.57.

5

Example 7:

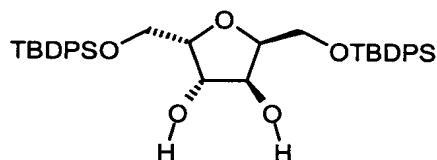
10 **2,3-bis-O-(Diphenylphosphino)-1,6-dideoxy-2,5-anhydro-D-mannitol (B7):** This product was prepared from **B4** in a similar manner to Example 5. Yield: 58% of theory.

15 $[\alpha]_D = -20.4$ (c 1.04, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ, 7.60-7.02 (m, 10H, Ph), 4.26 (m, 1H, H-3), 4.12 (m, 1H, H-2), 1.21 (d, 3H, J_{6,2}=6.4 Hz, H-6); ¹³C NMR (100.6 MHz, CDCl₃) δ, 142.12-127.08 (Ph), 90.74 (m, C-2), 78.35 (m, C-3), 19.15 (s, C-6); ³¹P NMR (161.974 MHz, CDCl₃) δ, 114.39 (s). Anal calcd for C₃₀H₃₀O₃P₂: C, 71.99; H, 6.04; found C, 72.22; H, 6.06.

20 **Example 8:**

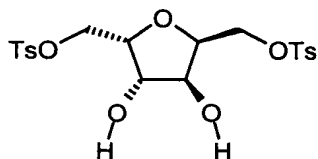
25 **1,6-di-O-(Triphenylmethyl)-2,5-anhydro-L-iditol (B8):** This product was prepared starting from 2,5-anhydro-L-iditol in a similar manner to Example 1.

^1H NMR (400 MHz, CHCl_3) δ , 7.60-7.02 (m, 15H, Ph), 4.42 (m, 1H, H-2), 4.25 (m, 1H, H-3), 3.48 (dd, 1H, $J_{6,2}=5.4$ Hz, $J_{6,6'}=9.6$ Hz, H-6), 3.40 (dd, 1H, $J_{6',2}=3.8$ Hz, $J_{6',6}=9.8$ Hz, H-6'); 3.24 (sa, 1H, OH), ^{13}C NMR (100.6 MHz) δ , 143.20.-127.01 (Ph), 87.20 ($\underline{\text{C}}(\text{Ph})_3$), 78.78 (C-2), 78.65 (C-3), 62.78 (C-6).

Example 9:

1,6-di-O-(*tert*-Butyldiphenylsilyl)-2,5-anhydro-L-iditol (B9): This product was prepared starting from 2,5-anhydro-L-iditol in a similar manner to Example 2.

^1H NMR (400 MHz, CDCl_3) δ , 7.81-7.32 (m, 10H, Ph); 4.26 (m, 1H, H-2); 4.38 (m, 1H, H-3); 4.07 (d, 1H, $J_{6,2}=4.4$ Hz, $J_{6,6'}=10.8$ Hz, H-6); 4.05 (d, 1H, $J_{6',2}=3.2$ Hz, $J_{6',6}=10.8$ Hz, H-6'); 3.99 (d, 1H, OH); 1.06 (s, 9H, $\text{C}(\underline{\text{CH}}_3)_3$); ^{13}C NMR (100.6 MHz) δ , 135.52-127.6 (Ph), 79.74 (C-2), 78.95 (C-3), 63.74 (C-6), 26.79 ($\text{C}(\underline{\text{C}}\text{H}_3)_3$), 19.19 ($\underline{\text{C}}(\text{CH}_3)_3$).

Example 10:

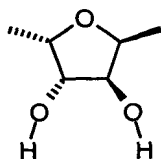
1,6-di-O-(*p*-Toluenesulphonyl)-2,5-anhydro-L-iditol (B10):

This product was prepared starting from 2,5-anhydro-L-iditol in a similar manner to Example 3.

¹H NMR (400 MHz, CDCl₃) δ, 7.83-7.21 (m, 4H, Ph); 4.42-3.91 (m, 5H, H-2, H-3, H-6, H-6', OH); 2.44 (s, 3H, CH₃); ¹³C NMR (100.6 MHz, CDCl₃) δ, 145.11-127.83 (Ph), 77.83 (C-2), 76.54 (C-3), 67.22 (C-6), 21.82 (CH₃).

Example 11:

1,6-Dideoxy-2,5-anhydro-L-iditol (B11):

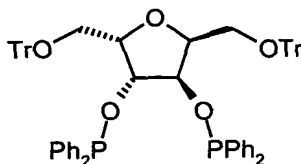


This product was prepared starting from **B10** in a similar manner to Example 4.

¹H NMR (400 MHz, CDCl₃) δ, 4.22 (m, 1H, H-2), 3.90 (m, 1H, H-3), 1.18 (d, 1H, J_{6,2} = 6.6 Hz, H-6); ¹³C NMR (100.6 MHz; CDCl₃) δ, 79.66 (C-2), 77.30 (C-3), 14.68 (C-6).

Example 12:

2,3-bis-O-(Diphenylphosphino)-1,6-di-O-(triphenylmethyl)-2,5-anhydro-L-iditol (B12).

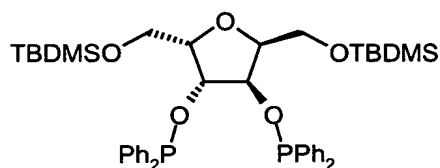


This product was prepared starting from **B8** in a similar manner to Example 5.

^1H NMR (400 MHz, CHCl_3) δ , 7.50-7.51 (m, 25H, Ph), 4.30 (m, 1H, H-2), 4.37 (m, 1H, H-3), 3.48 (dd, 1H, $J_{6,2} = 9.4$ Hz, $J_{6,6'} = 9.4$ Hz, H-6); 3.18 (dd, 1H, $J_{6',2} = 5.8$ Hz, $J_{6',6} = 9.4$ Hz, H-6') ^{13}C NMR (100.6 MHz) δ , 143.91-126.62 (Ph), 86.77 ($\text{C}(\text{Ph})_3$), 82.64 (m, C-3), 79.654 (d, C-2), 62.82 (s, C-6); ^{31}P NMR (161.974 MHz, CDCl_3) δ , 114.12 (s).

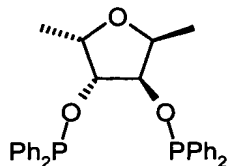
Example 13:

2,3-bis-*O*-(Diphenylphosphino)-1,6-di-*O*-(*tert*-butyldiphenylsilyl)-2,5-anhydro-L-iditol (B13):



This product was prepared starting from **B9** in a similar manner to Example 5.

^1H NMR (400 MHz, CDCl_3) δ , 7.81-7.09 (m, 20H, Ph), 4.51 (m, 1H, H-3), 4.21 (m, 1H, H-2), 3.85 (dd, 1H, $J_{6,2} = 7.4$ Hz, $J_{6,6'} = 10.0$ Hz H-6), 3.72 (dd, 1H, $J_{6',2} = 5.8$ Hz, $J_{6',6} = 10.0$ Hz, H-6'), 0.94 (s, 9H, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (100.6 MHz, CDCl_3) δ , 135.51-127.43 (Ph), 83.09 (m, C-3), 80.68 (d, C-2), 61.73 (s, C-6), 26.92 ($\text{C}(\text{CH}_3)_3$), 19.25 ($\text{C}(\text{CH}_3)_3$); ^{31}P NMR (161.974 MHz, CDCl_3) δ , 115.74 (s).

Example 14:**2,3-bis-O-(Diphenylphosphino)-1,6-dideoxy-2,5-anhydro-L-iditol (B14):**

5

This product was prepared starting from **B11** in a similar manner to Example 5.

10 ^1H NMR (400 MHz, CDCl_3) δ , 7.63-7.21 (m, 10H, Ph), 4.32 (m, 1H, H-2), 4.23 (m, 1H, H-3), 1.20 (d, 3H, $J_{6,2}=6.4$ Hz, H-6); ^{13}C NMR (100.6 MHz, CDCl_3) δ , 142.05-127.99 (Ph), 84.97 (m, C-3), 76.02 (m, C-2), 15.18 (s, C-6); ^{31}P NMR (161.974 MHz, CDCl_3) δ , 114.05 (s).

15 **Example 15:**

[Rh(cod)(B5)]BF₄ (B15): 0.030 g (0.073 mmol) of $[\text{Rh}(\text{cod})_2]\text{BF}_4$ was dissolved in 10 ml of CH_2Cl_2 . A solution of 0.090 g (0.088 mmol) of compound **B5** in 3 ml CH_2Cl_2 was added to the solution and the resulting solution was stirred for 30 min. The solvent was removed under reduced pressure and the crude product was washed with anhydrous hexane and with ethyl ether. Yield: 0.042 g (43% of theory).

25 $[\alpha]_D = +119.41$ (c 1.05, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ , 7.60-7.02 (m, 25H, Ph), 5.36 (m, 1H, H-3), 4.70 (m, 2H, CH(cod)); 4.47 (m, 1H, H-2), 3.58 (dd, 1H, $J_{6,2}=2.8$ Hz, $J_{6,6'}=10.8$ Hz, H-6), 3.18 (dd, 1H, $J_{6,2}=3.2$ Hz, $J_{6,6'}=10.8$ Hz, H-6'); 2.42-2.00 (m, 4H, $\text{CH}_2(\text{cod})$); ^{13}C NMR (100.6 MHz) δ , 144.10-126.05 (Ph, cod), 87.00 ($\underline{\text{C}}(\text{Ph})_3$), 82.67 (s, C-3), 82.45 (m, C-2),

63.33 (s, C-6); ^{31}P NMR (161.974 MHz, CDCl_3) δ , 122.61 (d, $J_{\text{P,Rh}} = 166.18$ Hz)).

Exempl 16:

5

[Rh(cod)(B6)]BF₄ (B16): This complex was prepared from **B6** in a similar manner to Example 15. Yield: 68% of theory.

10 $[\alpha]_{\text{D}} = (c, \text{CHCl}_3)$; ^1H NMR (400 MHz, CDCl_3) δ , 7.82-7.21 (m, 20H, Ph), 5.24 (m, 1H, H-3), 4.77 (m, 1H, CH(cod)); 4.67 (m, 1H, CH(cod)); 4.19 (m, 1H, H-2), 3.85 (dd, 1H, $J_{6,2} = 2.4$ Hz, $J_{6,6'} = 11.6$ Hz, H-6), 3.69 (dd, 1H, $J_{6,2} = 3.2$ Hz, $J_{6,6'} = 11.6$ Hz, H-6'); 2.41-2.20 (m, 4H, $\text{CH}_2(\text{cod})$); 1.04 (s, 9H, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (100.6 MHz, CDCl_3) δ , 134.10-126.07 (Ph, cod), 82.53 (m, C-2), 81.23 (s, C-3), 63.13 (s, C-6), 26.95 ($\text{C}(\text{CH}_3)_3$), 19.44 ($\text{C}(\text{CH}_3)_3$);

15 ^{31}P NMR (161.974 MHz, CDCl_3) δ , 125.136 (d, $J_{\text{P,Rh}} = 167.97$ Hz).

Example 17:

20 **[Rh(cod)(B7)]BF₄ (B17):** This complex was prepared starting from **B7** in a similar manner to Example 15. Yield: 55% of theory.

^1H NMR (400 MHz, CDCl_3) δ , 7.81-7.42 (m, 10H, Ph), 4.73 (m, 1H, CH(cod)); 4.64 (m, 1H, CH(cod)); 4.39 (m, 1H, H-3), 3.91 (m, 1H, H-2),); 2.61-2.20 (m, 4H, $\text{CH}_2(\text{cod})$); 1.13 (d, 3H, $J_{6,2} = 6.0$ Hz, H-6); ^{13}C NMR (100.6 MHz, CDCl_3) δ , 133.15-128.03 (Ph, cod), 85.76 (s, C-3), 75.68 (m, C-2), 18.64 (s, C-6); ^{31}P NMR (161.974 MHz, CDCl_3) δ , 127.39 (d, $J_{\text{P,Rh}} = 169.42$ Hz).

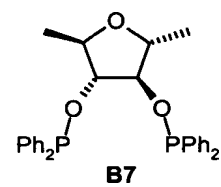
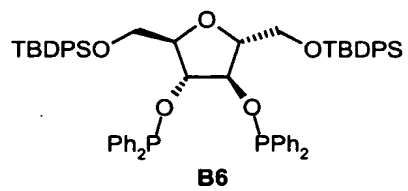
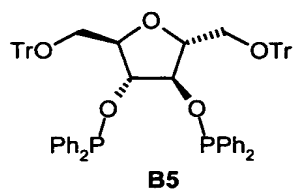
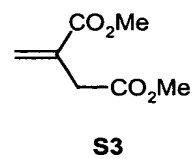
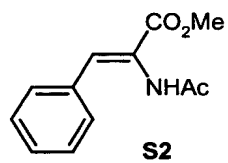
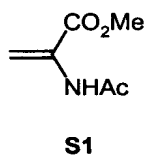
Example 18:

[Ir(cod)(B6)]BF₄ (B18): A solution of 102 mg (0.1 mmol) of compound **B6** in 2 ml of CH₂Cl₂ was added dropwise to a solution cooled to -80°C of 40 mg (0.08 mmol) of [Ir(cod)₂]BF₄ in 2 ml CH₂Cl₂. The resulting yellow solution was heated to 0°C and stirred for a further 15 minutes. The solvent was partly removed under reduced pressure, 30 ml of ethyl ether were added and the solids were filtered off and washed. Yield: 98.6 mg, 86% of theory.

¹H NMR (400MHz, CDCl₃) δ, 7.44-7.24 (m, 50H, CH arom), 5.35 (m, 2H, CH), 5.17 (m, 1H, CH); 4.52 (m, 2H, CH); 4.41 (m, 4H, CH₂); 3.60 (dd, J= 2.6 Hz, J= 10.4 Hz, 2H, CH₂), 3.21 (dd, J= 2.6 Hz, J= 10.4 Hz, 2H, CH₂), 2.42 (m, 2H, cod), 2.21 (m, 2H), 2.06 (m, 2H), 1.67 (m, 2H). ¹³C NMR (100.6 MHz) δ, 143.6 (C arom.), 132.4 (s, arom); 32.0 (s, arom); 131.7 (t, arom.), 131.2 (t, arom.), 129.1 (m, arom.), 128.7 (m, arom.), 128.68 (s, CH arom.), 128.1 (s, CH arom.), 127.4 (s, CH arom), 95.5 (s, CH), 83.3 (s, CH), 87.2 (s, C), 83.1 (s, CH), 82.4 (s, CH), 63.7 (CH₂), 31.3 (s, CH₂), 31.1 (s, CH₂). ³¹P NMR (161.9 MHz, CDCl₃) δ, 104.6.

Examples 19-41:**Rhodium-catalysed hydrogenation of enamides and methyl itaconate**

In a glass autoclave, 6.1 mg (0.015 mmol) of [Rh(cod)₂]BF₄ were dissolved in 15 ml of degassed CH₂Cl₂, 0.016 mmol of ligand and 1 mmol of substrate were added under nitrogen and hydrogenation was effected at room temperature and 1 atm of hydrogen pressure. Conversion and ee were determined by gas chromatography.

Ligands:**Substrates:**

The results of the hydrogenations are compiled in Table 1.

Table 1

Exam- ples	Sub- strate	Ligand	Solution (ml)	t (min)	Subst/R h (mol)	% conv.	%ee (R/S)
19	S1	B5	CH ₂ Cl ₂ 15	5	100	100	62(R)
20	S1	B5	CH ₂ Cl ₂ 15	35	500	93	67(R)
21	S1	B5	CH ₂ Cl ₂ 15	10	250	100	65(R)
22	S1	B5	MeOH 15	15	500	63	73(R)
23	S1	B5	acetone 15	15	500	99	75(R)
24	S1	B5	THF 15	15	500	36	63(R)
25	S1	B5	toluene/Me OH 15	15	500	59	65(R)
26	S1	B6	CH ₂ Cl ₂ 15	5	100	95	70(R)
27	S1	B6	CH ₂ Cl ₂ / acetone 2:13	5	100	100	85(R)
28	S1	B6	CH ₂ Cl ₂ / acetone 2:13	5	100	100	87(R)
29	S1	B6	CH ₂ Cl ₂ / acetone 2:13	15	100	100	90(R)
30	S1	B7	CH ₂ Cl ₂ 15	5	100	100	73(R)
31	S1	B7	CH ₂ Cl ₂ / acetone 2:13	5	100	100	79(R)
32	S2	B5	CH ₂ Cl ₂ 15	10	100	91	59(R)
33	S2	B5	Acetone 15	10	100	91	73(R)

Examp- les	Sub- strate	Ligand	Solution (ml)	t (min)	Subst/R h (mol)	% conv.	%ee (R/S)
34	S2	B6	CH ₂ Cl ₂ 15	5	100	98	73(R)
35	S2	B6	CH ₂ Cl ₂ / acetone 2:13	5	100	96	80(R)
36	S2	B7	CH ₂ Cl ₂ 15	5	100	100	72(R)
37	S2	B7	CH ₂ Cl ₂ / acetone 2:13	5	100	100	75(R)
38	S3	B5	CH ₂ Cl ₂ 15	15	100	100	48(S)
39	S3	B5	acetone 15	60	100	33	35(S)
40	S3	B6	CH ₂ Cl ₂ 15	15	100	96	48(S)
41	S3	B7	CH ₂ Cl ₂ 15	5	100	96	53(S)

Preparation of phosphine chlorides:

5 Examples 42-45:

Bis-(2,4-dimethylphenyl)chlorophosphine (B42): A solution of 2.92 ml (21.61 mmol) of 4-bromo-1,3-dimethylbenzene in 3 ml of Et₂O were added at 0°C to a suspension of 0.5 g (20.56 mmol) of magnesium turnings in 7 ml of THF and 7 ml of Et₂O and also a crystal of iodine. The mixture was heated to room temperature, stirred further overnight and slowly added dropwise at 0°C to a solution of 1.5 ml (10.31 mmol) of Et₂NPCl₂ in 8 ml of THF. The mixture was heated to room temperature and the solvent was subsequently removed under reduced pressure. After adding 60 ml of hexane, the mixture was filtered through Celite under argon and admixed with hydrogen chloride for 1 hour. After degassing, the resulting solids were filtered off under argon and dried. Yield: 1.4 g (58.3% of theory). ¹H

NMR (400 MHz, CDCl₃) δ , 7.40 (d, J_{meta} = 4.5 Hz, 2H, arom.), 7.2 (m, 4H, arom.), 2.5 (d, J_{PH} = 2.0 Hz, 6H, CH₃), 2.4 (s, 6H, CH₃). ³¹P NMR (161.974 MHz, CDCl₃) δ , 75.6.

5 **Example 43:**

Bis-(3,5-dimethylphenyl)chlorophosphine (B43): This product was prepared starting from 5-bromo-1,3-dimethylbenzene in a similar manner to Example 42. Yield: 47.2 % of theory. ¹H NMR (400 MHz, CDCl₃) δ , 7.2 (d, 4H, arom.), 7.01 (s, 2H, arom.), 2.37 (s, 12H, CH₃). ³¹P NMR (161.974 MHz, CDCl₃) δ , 83.7.

Example 44:

15 **Bis-(4-methoxyphenyl)chlorophosphine (B44):** This product was prepared starting from 1-bromo-4-methoxybenzene in a similar manner to Example 42. Yield 45% of theory. ¹H NMR (400 MHz, CDCl₃) δ , 7.48 (t, J_{orto} = 8.4 Hz, J_{PH} = 8.4 Hz, 4H, arom.), 6.88 (d, J_{orto} = 8.4 Hz, 4H, arom.), 3.75 (s, 6H, CH₃O). ³¹P NMR (161.974 MHz, CDCl₃) δ , 84.2.

20

Example 45:

Bis-(4-trifluoromethylphenyl)chlorophosphine (B45): This product was prepared starting from 1-bromo-4-(trifluoromethyl)benzene in a similar manner to Example 42. Yield 66% of theory. ¹H NMR (400 MHz, CDCl₃) δ , 7.33 (m, 8H, arom.). ³¹P NMR (161.9 MHz, CDCl₃) δ , 76.3.

30

Preparation of aminophosphines:**Exempl 46:**

5 **(Diethylamino)-bis(2,4-dimethylphenyl)phosphine (B46):** A solution of
2.92 ml (21.61 mmol) of 4-bromo-1,3-dimethylbenzene in 3 ml of Et₂O
were added at 0°C to a suspension of 0.5 g (20.56 mmol) of magnesium
turnings in 7 ml of THF and 7 ml of Et₂O and also a crystal of iodine. The
mixture was heated to room temperature, stirred further overnight and
10 slowly added dropwise at 0°C to a solution of 1.5 ml (10.31 mmol) of
Et₂NPCl₂ in 8 ml of THF. The mixture was heated to 5-10°C, stirred for a
further 2 hours and the solvent was subsequently removed under reduced
pressure. After adding 60 ml of hexane, the mixture was filtered through
Celite under argon and the solvent was subsequently removed under
15 reduced pressure. Yield: 1.37 g (59% of theory). ¹H NMR (400 MHz,
CDCl₃) δ, 6.9 (m, 6H), 3.03 (m, 4H, CH₂), 2.20 (s, 12H, CH₃), 0.81 (t,
³J=7.0 Hz, 6H, CH₃) ³¹P NMR (161.9 MHz, CDCl₃) δ, 47.8.

Example 47:

20 **(Diethylamino)bis(3,5-dimethylphenyl)phosphine (B47):** This product
was prepared starting from 5-bromo-1,3-dimethylbenzene in a similar
manner to Example 46. Yield 56.8% of theory. ¹H NMR (400 MHz, CDCl₃)
δ, 6.90 (d, 4H, arom.), 6.76 (s, 2H, arom.), 2.95 (m, 4H, CH₂), 2.11 (s,
25 12H, CH₃), 0.80 (t, ³J=7.0 Hz, 6H, CH₃). ³¹P NMR (161.9 MHz, CDCl₃) δ,
61.6.

Example 48:

30 **(Diethylamino)bis(4-methoxyphenyl)phosphine (B48):** This product
was prepared starting from 1-bromo-4-methoxybenzene in a similar

manner to Example 46. Yield: 57.2% of theory. ^1H NMR (400 MHz, CDCl_3) δ , 7.48 (dd, $J_{\text{orto}} = 8.8$ Hz, $J_{\text{PH}} = 6.4$ Hz, 4H, arom.), 6.88 (m, 4H, arom.), 3.81 (s, 6H, CH_3O), 3.06 (q, $^3J = 7.2$ Hz, 2H, CH_2), 0.96 (t, $^3J = 7.2$ Hz, 3H, CH_3). ^{31}P NMR (161.9 MHz, CDCl_3) δ , 59.5.

5

Example 49:

(Diethylamino)bis(4-trifluoromethylphenyl)phosphine (B49): This product was prepared starting from 1-bromo-4-(trifluoromethyl)benzene in a similar manner to Example 46. Yield: 61.4% of theory. ^1H NMR (400 MHz, CDCl_3) δ , 7.39 (m, 8H, arom.), 2.92 (m, 4H, CH_2), 0.82 (t, $^3J = 7.0$ Hz, 3H, CH_3). ^{31}P NMR (161.9 MHz, CDCl_3) δ , 61.5.

10

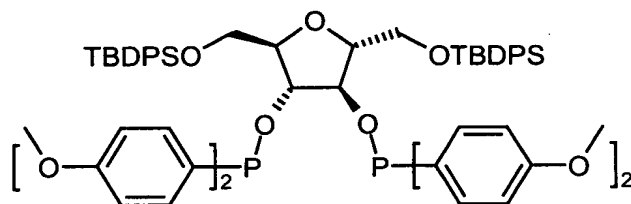
Preparation of biphosphorus compounds:

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Example 50:

2,3-bis-O-(Di(4-methoxyphenyl)phosphino)-1,6-di-O-(tert-butylidiphenylsilyl)-2,5-anhydro-D-mannitol (B50):

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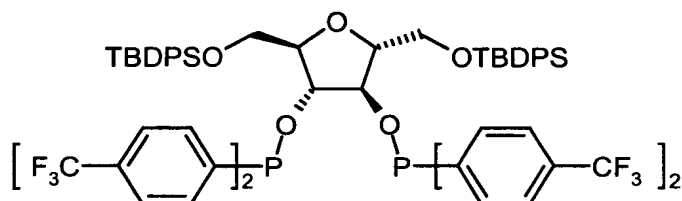
A mixture of 100 mg (0.156 mmol) of 1,6-di-O-(tert-butylidiphenylsilyl)-2,5-anhydro-D-mannitol (**B2**) and 109 mg (0.343 mmol) of diethylaminobis(p-methoxybenzene)phosphine (**B48**) in 2.2 ml of anhydrous toluene was stirred at 112°C overnight. After cooling, the solvent was removed under reduced pressure and the crude product was purified by means of column

25

chromatography. Yield: 40 mg (22.7% of theory). ^1H NMR (400 MHz, C_6D_6) δ , 7.93 (m, 8H, arom.), 7.67 (m, 8H, arom.), 7.26 (m, 12H, arom.), 6.84 (m, 8H, arom.), 5.38 (dd, $J=7.9$ Hz, $J=4$ Hz, 2H, CH), 4.59 (m, 2H, CH), 4.09 (dd, $J=10.9$ Hz, $J=4.2$ Hz, 2H, CH_2), 3.99 (dd, $J=10.9$ Hz, $J=4.2$ Hz, 2H, CH_2), 3.37 (s, 6H, CH_3O), 3.35 (s, 6H, CH_3O), 1.32 (s, 9H, CH_3), 1.27 (s, 9H, CH_3). ^{31}P NMR (161.9 MHz, C_6D_6) δ , 116.3.

Example 51:

2,3-bis-*O*-(Di((4-trifluoromethyl)phenyl)phosphino)-1,6-di-*O*-(*tert*-butyldiphenylsilyl)-2,5-anhydro-D-mannitol (**B51**):

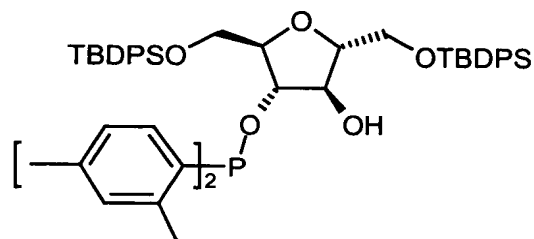


This product was prepared starting from 1,6-di-*O*-(*tert*-butyldiphenylsilyl)-2,5-anhydro-D-mannitol (**B2**) and (diethylamino)bis(4-trifluoromethylphenyl)phosphine (**B49**) in a similar manner to Example 50. Yield: 40 mg (28% of theory). ^1H NMR (400 MHz, C_6D_6) δ , 7.9 (m, 2H, arom.), 7.85 (m, 4H, arom.), 7.74 (m, 2H, arom.), 7.40-7.29 (m, 26H, arom.), 7.0 (m, 2H, arom), 5.36 (m, 2H, CH), 4.41 (m, 2H, CH), 4.02 (dd, $J=11.4$ Hz, $J=3.5$ Hz, 2H, CH_2), 3.79 (dd, $J=11.4$ Hz, $J=3.5$ Hz, 2H, CH_2), 1.28 (s, 9H, CH_3). ^{31}P NMR δ , (161.9 MHz, C_6D_6) 111.5.

Example 52:

25

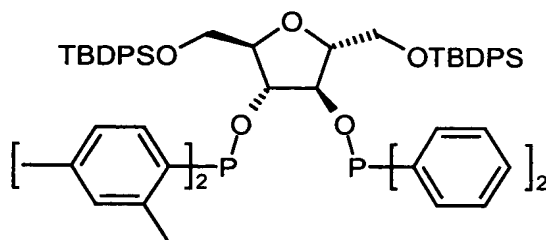
2-*O*-(Di(2,4-dimethylphenyl)phosphino)-1,6-di-*O*-(*tert*-butyldiphenylsilyl)-2,5-anhydro-D-mannitol (**B52**):



A solution of 337 mg (1.219 mmol) of bis-(2,4-dimethylphenyl)-
 5 chlorophosphine (**B46**) in 2 ml of anhydrous THF was added to a solution
 of 300 mg (0.468 mmol) of 1,6-di-*O*-(*tert*-butyldiphenylsilyl)-2,5-anhydro-D-
 mannitol (**B2**) and 0.26 ml of anhydrous Et₃N (1.86 mmol), and stirred at
 room temperature overnight. After adding ethyl ether, the mixture was
 filtered through Celite, solvent removed under reduced pressure and the
 10 crude product purified by means of column chromatography. Yield: 180
 mg (45% of theory). ¹H NMR (400 MHz, CDCl₃) δ, 7.59-6.87 (m, 26H,
 arom.), 4.47 (m, 1H, CH), 4.31 (m, 1H, CH), 3.99 (m, 2H, CH), 3.69 (m,
 3H, CH₂), 3.54 (dd, 1H, CH₂), 2.79 (s, OH), 2.30 (s, 3H, CH₃), 2.17 (s, 3H,
 CH₃), 2.11 (s, 3H, CH₃), 2.06 (s, 3H, CH₃), 0.96 (s, 9H, CH₃), 0.94 (s, 9H,
 15 CH₃). ¹³C NMR (75.4 MHz, CDCl₃) δ, 138.1-127.6 (CH, C, arom.), 86.0
 (²*J*_{C-P}=18 Hz, CH), 84.9 (CH), 83.9 (³*J*_{C-P}=6.13 Hz, CH), 78.0 (²*J*_{C-P}=4.5
 Hz, CH CH), 64.7 (CH₂), 64.1 (CH₂), 27.1 (CH₃), 27.0 (CH₃), 21.4 (C), 20.5
 (d, ³*J*=48.4 Hz, CH₃), 20.3 (d, ³*J*=48.4 Hz, CH₃), 19.6 (s, CH₃), 19.5 (s,
 20 CH₃). ³¹P NMR (161.9 MHz, CDCl₃) δ, 102.9.

Example 53:

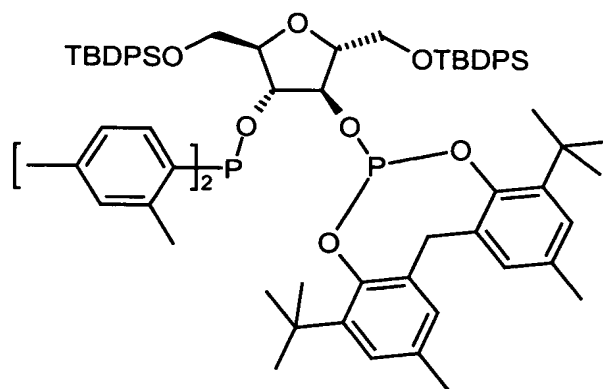
**2-*O*-(2,4-dimethylphenylphosphino)-3-*O*-(diphenylphosphino)-1,6-di-
 25 *O*-(*tert*-butyldiphenylsilyl)-2,5-anhydro-D-mannitol (**B53**):**



A solution of 0.0125 ml (0.066 mmol) of chlorodiphenylphosphine was added to a solution of 58 mg (0.06 mmol) of 2-O-(2,4-dimethylphenylphosphino)-1,6-dideoxy-2,5-anhydro-D-mannitol (**B52**) and 0.032 ml (0.23 mmol) of anhydrous Et₃N in 0.5 ml of anhydrous THF. The mixture was heated to room temperature and stirred further overnight. After adding degassed, anhydrous hexane, the mixture was filtered through Celite, the solvent removed under reduced pressure and the crude product purified by means of column chromatography. Yield 29.4 mg (45.9% of theory). ¹H NMR (400 MHz, CDCl₃) δ, 7.67-6.91 (m, 36H, arom.), 4.8 (m, 2H, CHx2), 4.15 (m, 2H, CHx2), 3.73 (m, 2H, CH₂), 3.59 (m, 2H, CH₂), 2.25 (s, 3H, CH₃), 2.23 (s, 3H, CH₃), 2.19 (s, 3H, CH₃), 2.14 (s, 3H, CH₃), 1.1 (s, 9H, CH₃), 1 (d, 9H, CH₃). ³¹P NMR (161.9 MHz, C₆D₆) δ, 114.1, 102.7.

Example 54:

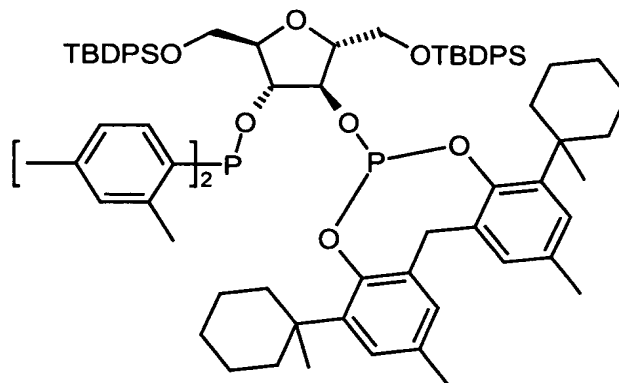
2-O-(2,4-Dimethylphenylphosphino)-3-O-(4,8-di-tert-butyl-2,10-dimethyl-12H-dibenzo[δ,γ][1,3,2]dioxaphosphocino)-1,6-di-O-(tert-butyldiphenylsilyl)-2,5-anhydro-D-mannitol (B54):



A solution of 100 mg (0.52 mmol) of 4,8-di-*tert*-butyl-6-chloro-2,10-dimethyl-12*h*-dibenzo[δ,γ][1,3,2]dioxaphosphocine and 0.100 ml (1.23 mmol) of anhydrous pyridine in 1 ml of anhydrous toluene was added dropwise at 0°C to a solution of 178 mg (0.202 mmol) of 2-*O*-(2,4-dimethylphenylphosphino)-1,6-di-*O*-(*tert*-butyldiphenylsilyl)-2,5-anhydro-D-mannitol (**B52**) and 0.100 ml (1.23 mmol) of anhydrous pyridine in 1 ml of anhydrous toluene. The mixture was heated to room temperature and stirred further overnight. After adding degassed, anhydrous hexane, the mixture was filtered through Celite, the solvent removed under reduced pressure and the crude product purified by means of column chromatography. Yield 100 mg (39.6% of theory). ^1H NMR (400 MHz, C_6D_6) δ , 7.97-6.38 (m, 30H, arom.), 5.50 (m, 1H, CH), 5.21 (m, 1H, CH), 4.83 (m, 1H, CH), 4.53 (d, $J=10.4$ Hz, 1H, CH_2), 4.50 (m, 3H, CH, CH_2), 4.39 (dd, 1H, $J=10.8$ Hz, $J=5.59$ Hz, CH_2), 4.15 (dd, 1H, $J=10.8$ Hz, $J=5.59$ Hz, CH_2), 3.3 (d, $J=10.4$ Hz, 1H, CH_2), 2.59 (s, 3H, CH_3), 2.51 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.12 (s, 6H, CH_3), 2.1 (s, 3H, CH_3), 1.54 (s, 9H, CH_3), 1.53 (s, 9H, CH_3), 1.36 (s, 9H, CH_3), 1.32 (s, 9H, CH_3). ^{31}P NMR (161.9 MHz, C_6D_6) δ , 128.8, 103.6.

Example 55:

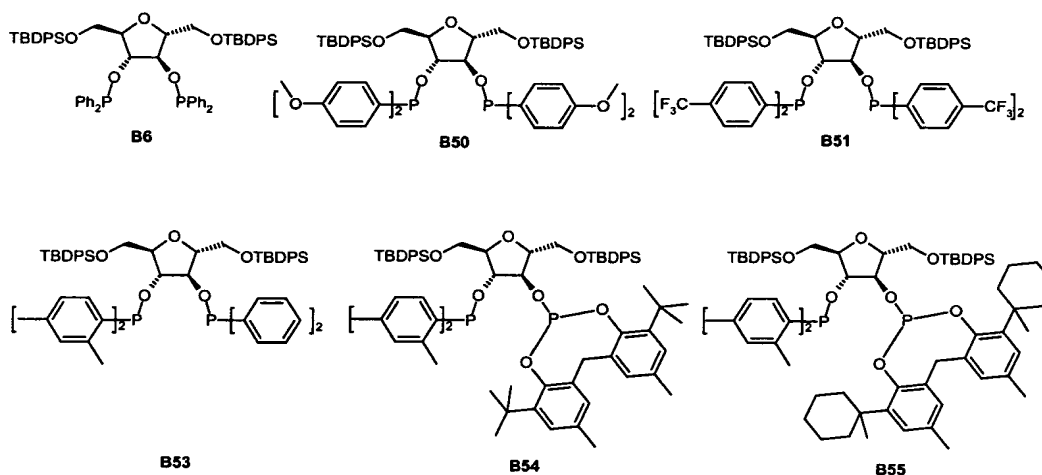
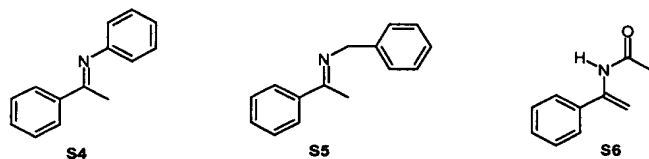
2-*O*-(2,4-Dimethylphenylphosphino)-3-*O*-(2,10-dimethyl-4,8-bis(1-methylcyclohexyl)-12H-dibenzo[δ,γ][1,3,2]dioxaphosphocino)-1,6-di-
 5 *O*-(*tert*-butyldiphenylsilyl)-2,5-anhydro-D-mannitol (**B55**):



This product was prepared starting from 2-*O*-(2,4-
 10 dimethylphenylphosphino)-1,6-di-*O*-(*tert*-butyldiphenylsilyl)-2,5-anhydro-D-mannitol (**B52**) and 6-chloro-2,10-dimethyl-4,8-bis(1-methylcyclohexyl)-12H-dibenzo[δ,γ][1,3,2]-dioxaphosphocine in a similar manner to Example 54. Yield 71 mg (32.4% of theory). ^1H NMR (400 MHz, C_6D_6) δ , 7.99-6.3 (m, 30H, arom.), 5.44 (m, 1H, CH), 5.14 (m, 1H, CH), 4.81 (m, 1H, CH),
 15 4.57 (dd, $J=10.7$ Hz, $J=4.5$ Hz, 1H, CH_2), 4.53 (m, 1H, CH, CH_2), 4.41 (dd, 1H, $J=10.7$ Hz, $J=4.5$ Hz, CH_2), 4.29 (dd, 1H, $J=10.8$ Hz, $J=5.0$ Hz, CH_2), 4.18 (dd, 1H, $J=10.8$ Hz, $J=5.0$ Hz, CH_2), 3.3 (d, $J=12.7$ Hz, 1H, CH_2), 2.59 (s, 3H, CH_3), 2.52 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 1.68-1.57 (m, CH_2), 1.48 (s, 3H, CH_3),
 20 1.47 (s, 3H, CH_3), 1.36 (s, 9H, CH_3), 1.33 (s, 9H, CH_3). ^{31}P NMR (161.9 MHz, CDCl_3) δ , 128.7, 105.3.

Iridium-catalysed hydrogenation of imines and enamides**Examples 56-78:**

- 5 0.01 Molar equivalent of transition metal compound and 0.012 molar equivalent of ligand were dissolved under argon in degassed CH_2Cl_2 (0.015 M) and stirred at room temperature for 1/2 hour. After adding one molar equivalent of substrate in degassed CH_2Cl_2 (0.15 M) under argon, the mixture obtained was hydrogenated in an autoclave at the appropriate
- 10 temperature under hydrogen pressure. Conversion and ee were determined by chromatography.

Ligands:**Substrates:**

15

The results of the hydrogenations are compiled in Table 2.

Table 2

Ex- am- pl s	Sub- stra- t s	Lig- and	Metal precursor	Addi- tive	T (°C)	P (bar)	Time (h)	Sub- strate/ metal (mol)	Con- v r- sion (%)	ee (%)
56	S4	B6	[Ir(cod) ₂]BF ₄	-	25	70	16	100	100	65
57	S4	B51	[Ir(cod) ₂]BF ₄	-	25	70	16	100	100	31
58	S4	B50	[Ir(cod) ₂]BF ₄	-	25	70	16	100	97	71
59	S4	B50	[Ir(cod) ₂]BF ₄	4% phthal- imide	25	70	16	100	99	70
60	S4	B50	[Ir(cod) ₂]BF ₄	4% BzNH ₂	25	70	16	100	41	52
61	S5	B54	[Ir(cod) ₂]BF ₄	-	25	70	16	100	86	73
62	S5	B54	[Ir(cod) ₂]BF ₄	-	25	70	0.5	100	24	68
63	S5	B54	[Ir(cod) ₂]BF ₄	-	0	70	2	100	4	40
64	S5	B54	[Ir(cod) ₂]BF ₄	10% I ₂	0	70	2	100	1	76
65	S5	B54	[Ir(cod) ₂]BF ₄	-	50	70	0.5	100	80	61
66	S5	B54	[Ir(cod) ₂]BF ₄	10% phthal- imide	25	70	16	100	89	75
67	S5	B54	[Ir(cod) ₂]BF ₄	10% BzNH ₂	25	70	16	100	91	75
68	S5	B55	[Ir(cod) ₂]BF ₄	10% phthal- imide	25	70	16	100	63	54
69	S5	B55	[Ir(cod) ₂]BF ₄	10% BzNH ₂	25	70	16	100	81	58
70	S6	B6	[Rh(nbd) ₂]P F ₆	-	25	3.5	24	100	100	48
71	S6	B51	[Rh(nbd) ₂]P F ₆	-	25	3.5	24	100	99	6

Ex- am- pl s	Sub- stra- t s	Lig- and	Metal pr cursor	Addi- tive	T (°C)	P (bar)	Time (h)	Sub- strate/ metal (mol)	Con- ver- sion (%)	ee (%)
72	S6	B50	[Rh(nbd) ₂]P F ₆	-	25	3.5	24	100	100	33
73	S6	B53	[Rh(nbd) ₂]P F ₆	-	25	3.5	24	100	98	20
74	S6	B54	[Rh(nbd) ₂]P F ₆	-	25	3.5	24	100	97	22
75	S6	B6	[Rh(nbd) ₂]P F ₆	-	25	3.5	24	100	56	40
76	S6	B51	[Rh(nbd) ₂]P F ₆	-	25	3.5	24	100	89	50
77	S6	B50	[Rh(nbd) ₂]P F ₆	-	25	3.5	24	100	89	28
78	S6	B54	[Rh(cod) ₂]B F ₄	-	25	3.5	24	100	98	27

Example 79

5 In an autoclave, 28.1 mg (0.022 mmol) of [Ir(cod)(B6)]BF₄ (**B18**) and 0.39 g (2 mmol) *N*-(phenylethylidene)aniline (**S4**) were dissolved in 10 ml of degassed CH₂Cl₂. The mixture was hydrogenated at room temperature and 50 bar of hydrogen pressure. Conversion and ee were determined by gas chromatography. 99% conversion, 67% ee.

10 Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.